

## MECHANISM OF HYDROTREATING REACTIONS: SOLID ACID CATALYSIS

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### ABSTRACT

Acid catalysis of coal liquefaction has been extensively studied with both solid and liquid forms of catalysts. Zinc chloride has been utilized in the molten state, complexed with methanol, and supported on silica gel and other materials. This paper addresses the differences between the mechanistic pathways occurring in these various states. Thermal studies of the silica gel-supported zinc chloride demonstrate a change from Lewis to Brønsted acidity with increasing temperature. The major pathway for silica gel-supported zinc chloride is Brønsted acid catalysis, but some Lewis acid activity is found. Since hydrogen does not add directly to the primary carbonium ion intermediates involved in hydrodealkylation of alkylarenes, the role of hydrogen in driving the reaction to the cracked products rather than condensation is being investigated.

Key Words: Brønsted acidity, solid acid catalyst, oligomer

### INTRODUCTION

Conversion of coal to a liquid product with an acid catalyst has been extensively investigated in the last quarter century. A liquefaction process which utilized molten zinc chloride as an acid catalyst was developed by Consolidation Coal Company (1). Fundamental studies of the chemistry of zinc chloride-catalyzed liquefaction were pursued at Berkeley and other laboratories. Zinc chloride is a mild Lewis acid, and under anhydrous conditions was not able to effectively catalyze the cleavage of aryl-alkyl bonds at moderate temperatures (325°C) unless the rings were highly activated (2). Complexation of zinc chloride with methanol, water, or hydrogen halide gave catalysts with proton-donating potential (Brønsted acidity) that were able to catalyze hydrocracking more effectively (3). Reactions with dibenzylether at 325°C gave products that could have resulted from Lewis acid catalysis of cleavage of C-O bond (4); however, hydrogen chloride, which formed as a reaction product from the ether caused rapid cleavage of the ether when combined with the zinc chloride.

We have recently developed effective catalysts for coal hydrotreatment in which zinc chloride is complexed to solid supports. Zinc chloride bonded to silica gel or clay supports have been found to effectively catalyze cleavage reactions and remove heteroatoms from model compounds (5,6) as well as coal liquids (7,8).

This paper reports our work on the characterization of acidic sites of the silica gel-supported zinc chloride catalysts. Reactions with model compounds confirmed the mechanistic implications of these studies.

### EXPERIMENTAL

#### Catalyst Preparation

Silica gel-supported zinc chloride catalysts, SZC-50 (50 wt.% zinc chloride-loaded silica gel) and SZC-16 (16 wt.% zinc chloride-loaded silica gel) were prepared as described earlier (5).

## Characterization of Solid Acid Catalysts

### Acidity Measurements

Surface acidity of the solid acid catalysts was determined by pyridine adsorption and desorption using infrared and thermogravimetric analyses.

#### Infrared Method

A small amount of sample (100 mg) was placed in a glass chamber attached to a vacuum pump, gas inlet, and a gas outlet. The chamber was evacuated, and argon saturated with pyridine was introduced into the chamber until the weight increase ceased. At this stage, the chamber was evacuated until the physisorbed pyridine was removed as indicated by the constant weight of the base absorbed sample. The infrared spectra of the pyridine-absorbed catalyst was obtained in KBr on a Nicolet 20SXB FTIR spectrometer with diffused reflectance cell, equipped with a mercury cadmium telluride (MCTA) detector, and a Nicolet 1280 computer with a fast Fourier transform coprocessor. The pyridine-absorbed catalyst was heated in vacuo at several temperatures, and infrared spectrum was recorded for the residue formed at each temperature.

#### Thermogravimetric Method

Approximately 20 mg of catalyst were placed on the sample pan of the DuPont 951 thermogravimetric balance module which was interfaced with a DuPont 1090 thermoanalyzer (controller and data station). The sample was purged at ambient temperature with argon until constant weight was achieved (several minutes). The argon flow was then stopped, and the sample chamber was evacuated. The vacuum pump continued to hold the partial vacuum until constant weight was once again achieved. The pump was then turned off, and a flow of pyridine-saturated argon at ambient temperature was introduced into the sample chamber. The pyridine-argon flow continued for 180 minutes at which time the weight gained by the sample had nearly ceased. The chamber was again evacuated, still at ambient temperature, and held under partial vacuum for 40 minutes. When constant weight was achieved, the temperature was increased at 20°C/min to 105°C where it was held for 30 minutes. The temperature was then increased at 2°C/min to 202°C and held there for 30 minutes, followed by a temperature increase at 20°C/min to 300°C where it was held for 60 minutes. Upon reaching constant weight, the experiment was terminated.

#### Hydrotreating Reactions

The details of experimental procedures used for the hydrotreating reactions are available in the reports published in the literature (5-9). The method of Vogel (10) was used for chlorine analysis.

## RESULTS AND DISCUSSION

Elemental analyses of the zinc (II) chloride mixtures with silica gel obtained from the reaction in carbon tetrachloride and THF indicated that a small amount of chloride loss occurred during the heating procedure. Most of the salt (98%) was present, and only a small amount of chlorine was present as Si-O-ZnCl. The catalyst was a mixture of zinc chloride, zinc chloride complexed with silica gel, and oxyzinc salt.

Previous results from Hammett acidity studies at ambient temperature for SZC-50 indicated that highly acidic sites are present in this catalyst (6). Coordination of zinc chloride to surface silica hydroxyls on the silica gel-supported catalyst will be expected to generate new acidic sites of both Lewis and Brönsted types. The nature of these sites in the SZC-50 and SZC-16 catalysts at both ambient and higher temperatures is elucidated by the present study.

Infrared spectroscopy of the pyridine complex was used to determine the relative proportion of Lewis and Brönsted acid sites in the silica gel-zinc chloride catalysts. In the infrared spectrum of the pyridine-adsorbed catalyst, the bands around 1440 and 1536  $\text{cm}^{-1}$  are assigned to the pyridine-Lewis acid coordination bond and the pyridine-Brönsted acid bond respectively. The relative intensities of these bands were converted to the concentration ratio by using the respective extinction coefficients. In the SZC-16 catalyst, very few Brönsted acid sites were present at ambient temperature. However, on heating the pyridine complex of SZC-16 at several temperatures (25–200°C) for 1 hour, the intensity of the band due to the pyridine-Brönsted acid bond increased (Table 1). The increase in the intensity of the Brönsted band must be due to creation of new strong Brönsted acid sites as the temperature increases. This process is accompanied by the loss of pyridine from that portion of the Lewis sites that are weakly acidic. Thus, there is a continuing decrease in the Lewis band, and corresponding decrease in the ratio of the concentration of Lewis sites to Brönsted sites with temperature. Table 1 also gives the calculated ratios from the absorbance data from the SZC-16 sample and extinction coefficients for the bands.

At ambient temperature, the ratio of the concentration of Lewis sites to Brönsted sites for the SZC-50 was 3.4. This lower ratio of Lewis/Brönsted acid sites in the SZC-50, which corresponds to a larger concentration of Brönsted sites, is likely due to increased electron-withdrawing effects of the greater number of zinc chloride moieties coordinated with the silica hydroxyls.

TABLE 1  
INFRARED ABSORBANCE OF PYRIDINE-ADSORBED SZC-16

| Temp<br>(°C) | Absorbance                               |  | Lewis/Brönsted Sites |
|--------------|--|--|----------------------|
|              | 1440 $\text{cm}^{-1}$ Band<br>(L-P Band) | 1536 $\text{cm}^{-1}$ Band<br>(B-P Band) |                      |
| 25           | 0.181                                    | 0.01                                     | 12.46                |
| 100          | 0.184                                    | 0.022                                    | 8.52                 |
| 150          | 0.129                                    | 0.027                                    | 4.78                 |
| 200          | 0.043                                    | 0.018                                    | 2.39                 |

A thermogravimetric technique was also used to determine the total acid sites and stability of the catalyst. In the TGA experiment, the weight of the catalyst increased by 41.62 and 12.13 wt% for SZC-50 and SZC-16 catalysts respectively, upon pyridine absorption followed by evacuation at ambient temperature. The weight increase is due to the chemical reaction of the pyridine at both Lewis and Brönsted acid sites and, therefore, is a measure of the total acidity of the catalyst. The total acidity for SZC-50 and SZC-16 is 5.04 and 1.75 meq/g catalyst respectively.

Upon slowly heating the catalyst (2°C/min) to 300°C, all of the adsorbed pyridine could be removed. Heating above 300°C resulted in the loss of chlorine due to decomposition and or sublimation of zinc chloride from the catalyst surface.

#### Catalytic Hydrotreating of Model Compounds:

Reactions of model compounds such as bibenzyl, diphenyl sulfide, dibenzothiophene, cumene, 1-phenyldecane, n-hexadecane, and p-cresol with supported zinc chloride catalysts gave products indicative of a carbonium ion mechanism (5,6). The formation/conversion of acidic sites on the SZC catalyst to Bronsted acids at higher temperatures such as those useful in hydrotreating reactions has not yet been studied. However, we may speculate that at higher temperatures, significant numbers of Bronsted sites are present, and these sites are responsible for the majority of catalytic effects in cleavage of alkylarenes at temperatures between 300 and 400°C. Several experiments were carried out to identify whether Lewis or Bronsted catalysis is predominant at these temperatures with various related materials.

The reaction of bibenzyl in molten zinc chloride (ZC-melt) was carried out under conditions similar to those used for SZC catalysts, and a poor conversion was obtained (Table 2). This result is consistent with the earlier study of Bell (2), that demonstrated the poor catalytic ability of zinc chloride for hydrocracking when restricted to only Lewis acidity (no added hydroxy compound). A reaction conducted with silica gel (SG, no zinc chloride) gave a very poor conversion, consistent with the weak acidity of the silica hydroxyls. When the reaction was carried out with silica gel-zinc chloride (50% zinc chloride) catalyst, 85% of bibenzyl was converted into products. The major products were benzene, ethylbenzene and a small amount of toluene. The ratio of benzene to ethylbenzene was 3. In addition, 18% of the starting material was converted into oligomers. No coke formation occurred under these conditions. The conversion and product distribution from the reaction of bibenzyl with SZC-16 was comparable with that obtained from SZC (50% zinc chloride loaded silica gel). These results suggest that 16% zinc chloride loading on silica gel may be adequate for optimum catalytic activity.

The most likely mechanism for the reaction of bibenzyl with the SZC catalyst is the same as that proposed for the zinc chloride-hydroxyl or zinc chloride-hydrogen chloride complex suggested earlier (2) to account for the formation of ethylbenzene and benzene at temperatures in the 300°C regime. This mechanism proceeds via ipso protonation followed by cleavage of the aryl-alkyl bond to form the phenylethyl carbonium ion intermediate. The carbonium ion is then reduced to the alkyl group. Ethylbenzene is further cracked to benzene via the same steps, the extent depending on the activity of the catalyst.

The effect of molecular hydrogen on the conversion of bibenzyl and the product distribution was investigated by carrying out reactions both in the presence and absence of hydrogen. The percent conversion measured as the disappearance of the substrate was almost the same in both these reactions. However, the product distribution was significantly affected by the presence of hydrogen (Table 2). The reaction with no hydrogen produced 7% of coke which is formed due to retrograde condensation reactions. Also the amount of condensation products (substituted bibenzyls) increased from 18% to 27% in the absence of hydrogen. In the presence of hydrogen the amount of benzene was only slightly higher, but the amount of ethylbenzene increased considerably. In the reaction mechanism postulated above, the phenylethyl carbonium ion can undergo a variety of reactions (Figure 1) to give

TABLE 2  
CATALYTIC HYDROCRACKING OF BIBENZYL

Reaction Temp. = 350°C, Reaction Time = 3 Hrs, 5.49 mmols Bibenzyl

| Catalyst<br>(g)   | Hydrogen<br>(psig) | Conversion<br>(%) | Major Products<br>(mmols)   |
|-------------------|--------------------|-------------------|---|
| SG<br>(0.25)      | Hydrogen<br>1000   | 2                 | Benzene (tr.)<br>Ethylbenzene (tr.)<br>Toluene (tr.)                                      |
| ZC-melt<br>(0.25) | Hydrogen<br>1000   | 13                | Benzene (0.08)<br>Ethylbenzene (0.04)<br>Toluene (0.02)                                   |
| SZC-50<br>(0.5)   | Hydrogen<br>1000   | 85                | Benzene (3.54)<br>Ethylbenzene (1.35)<br>Toluene (0.15)<br>Cond. Prod. (18%)<br>Coke (0%) |
| SZC-50<br>(0.5)   | None               | 83                | Benzene (3.2)<br>Ethylbenzene (0.8)<br>Toluene (0.2)<br>Cond. Prod. (27%)<br>Coke (7%)    |
| SZC-50<br>(0.5)   | Deuterium<br>1000  | 64                | Benzene (2.6)<br>Ethylbenzene (1.1)<br>Toluene (0.1)<br>Cond. Prod. (24%)<br>Coke (0%)    |
| SZC-16<br>(0.5)   | Hydrogen<br>1000   | 75                | Benzene (3.12)<br>Ethylbenzene (0.9)<br>Toluene (0.2)                                     |

ethylbenzene product. The fact that ethylbenzene forms even in the absence of molecular hydrogen indicates that hydride transfer from Scholl intermediates or hydroaromatic condensation products is the major mechanism for formation of ethylbenzene. Hydrogen may be indirectly involved through reductions of these condensation products.

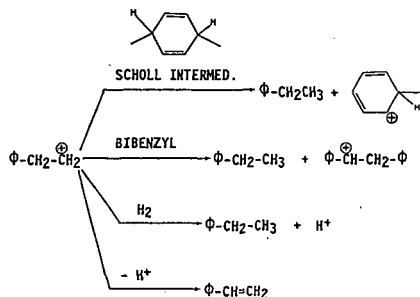


Figure 1. Reactions of Phenylethyl Carbonium Ion

When hydrogen was replaced with deuterium, the conversion was somewhat lower. This is very likely the result of an isotope effect that reduces the rate of hydrogenation of the Scholl intermediates or the rate of transfer of hydrogens from the hydrogenated Scholl intermediates to the carbonium ion intermediates.

1,3-Diphenylpropane (DPP) and neopentylbenzene (NPB) were also used to investigate the catalysis mechanism of silica gel-zinc chloride. The reactions were carried out at 350°C for 3 hours in the presence of 1000 psig of hydrogen. Major products and the percent conversion for these reactions are presented in Table 3. 1,3-diphenylpropane gave benzene and indan as the major products. The formation of these products requires no hydrogen or reduction, only the Brønsted acid catalyst. Ipso protonation of the aromatic ring, followed by aryl-methylene bond cleavage gives the phenylpropyl carbonium ion, that undergoes cyclization to give indan as the second major product. The minor products from this reaction were C<sub>1</sub>-C<sub>3</sub> benzenes. These products probably result from other mechanism involving Lewis acid catalysis.

The conversion of neopentylbenzene was much lower than that of diphenylpropane, and a variety of products were obtained. The major product from this reaction was benzene, which again is formed by the ipso protonation of the aromatic ring followed by aryl-methylene bond cleavage. Neopentyl carbonium ion rearranged to produce 2-methylbutane (Figure 2). Toluene and 2-methylpropane may have been formed from the Lewis acid-catalyzed cracking of neopentylbenzene.

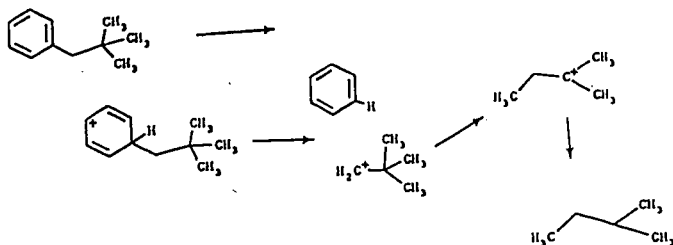


Figure 2. Brønsted Acid-Catalyzed Mechanism  
TABLE 3

#### CATALYTIC HYDROCRACKING OF 1,3-DIPHENYLPROPANE AND NEOPENTYL BENZENE

Reaction Temp. = 350°C, Reaction Time = 3 HRS  
Catalyst wt./substrate wt. = 0.5,  $H_2$  = 1000 psig

| Catalyst<br>(g)  | Substrate<br>(mmols) | Conv.<br>(%) | Major Products<br>(mmols)  |
|------------------|----------------------|--------------|--|
| SZC-50<br>(0.25) | DPP<br>(2.6)         | 76           | Indan (1.39)<br>Propylbenzene (0.08)<br>Ethylbenzene (0.06)<br>Toluene (0.05)<br>Benzene (2.43)<br>Cond. Prod. (0%)<br>Coke (0)%   |
| SZC-50<br>(0.25) | NPB<br>(3.5)         | 26           | Benzene (0.29)<br>2-Methylbutane (0.08)<br>2,2-Dimethylpropane (0.003)<br>Toluene (0.06)<br>2-Methylpropane (0.04)<br>Butane (0.003)<br>Pentane (0.001)<br>Ethylbenzene (0.03) |

#### CONCLUSIONS

SZC catalysts contain fewer Brønsted acid sites at ambient temperature, but these sites increase at higher temperatures. At the hydrotreating temperatures, the cleavages of aryl-alkyl bonds are Brønsted acid-catalyzed. Hydrogen is not required for hydrocracking reactions, but prevents coking reactions.

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